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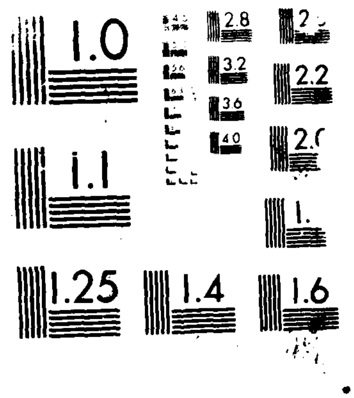
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OFFICE OF NAVAL RESEARCH

FINAL REPORT

Contract N00014-82-K-0523

R&T Code: 413a003-3

July 1, 1982 to March 31, 1989

# HIGH TEMPERATURE SOLAR ELECTROTHERMAL PROCESSING

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# HIGH TEMPERATURE SOLAR THERMOCHEMICAL PROCESSING

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d. Brief Description of Project:

Chemical transformation at a given temperature and pressure requires a total energy input, $\Delta H$ of the chemical reaction. The minimum amount of energy which must be supplied as (electrical) work is $\Delta G$ of the reaction. The rest may be supplied as process heat or as work. Since $\Delta H$ of most chemical reactions is relatively independent of temperature, and $\Delta G$ decreases with temperature, there is an energy advantage in conducting electrolytic separations at high temperatures. At sufficiently high temperatures all of the necessary energy may be solar process heat, replacing all of the electrical energy input, as we have experimentally observed. We conducted analytical and experimental studies of high temperature electrolysis in a highly concentrating solar furnace as well as in an electric furnace. We sought and found suitable materials for the construction of electrodes and cells and appropriate reactions which will acquire technological significance, designed and built receivers for sunlight and reactors which can interface with them, acquired operating experience with them, and conducted electrochemical and thermochemical measurements.

e. Significant Results

During the course of this study we have demonstrated the solarthermal assisted electrolysis of zinc oxide using non-reacting anodes as well as graphite anodes and the direct solarthermal reduction of zinc oxide by graphite to produce zinc. We also studied the electroreduction of magnesium oxide in a solar furnace and in an electric furnace. We designed, constructed, and tested a new kind of solar receiver-reactor. Its material cost is 1/20 of previous devices. The labor cost is minimal. Since it has a very low thermal inertia it can quickly be brought to the operating temperature and is well suited for solar thermochemical studies. With it we have solarthermally produced titanium carbide by the solarthermal reduction of titanium dioxide with carbon, zinc by the direct reduction of zinc oxide with carbon, and magnesium and possibly magnesium carbide by the direct solarthermal reduction of magnesium oxide with

carbon. We have also constructed and studied an apparatus which makes use of a zirconia membrane for the electrolytic separation of oxygen from zinc oxide vapor for the production of zinc, and in the process measured the effective electrical conductances and their variation with temperature of slip cast zirconia tubes in the transport of oxygen, and are attempting to make a two membrane device for the solar thermochemical or solar thermoelectrochemical splitting of water into hydrogen and oxygen. In a related study, which was funded primarily by NSF but also received some support from ONR, we demonstrated the activation of glassy carbon anodes which made it possible to overcome the fouling of electrodes in the anodic oxidation of sulfide, a major roadblock to the development of a process for electrolyzing hydrogen sulfide for the production of hydrogen and sulfur from it. The work done under this contract has been reported in a series of 13 technical reports to ONR.

f. Reviewed archives journal publications resulting in whole or in part from ONR supported research.

1. Edward A. Fletcher and Jon E. Noring, "High-Temperature Solar Electrothermal Processing-- Zinc from Zinc Oxide," Energy <u>8</u>, 247(1983).

2. Edward A. Fletcher, "Hydrogen and Sulfur from Hydrogen Sulfide II. Ambient Temperature Electrolysis Using Oxidation of Hydrogen Sulfide by Air as the Prime Energy Source," Energy <u>8</u>, 835(1983).

3. R.B. Diver, S. Pederson, T. Kappauf, and E.A. Fletcher, "Hydrogen and Oxygen from Water VI. Quenching the Effluent from a Solar Furnace," Energy <u>8</u>, 947(1983).

4. D.E.E. Carlson, R.B. Diver,, and E.A. Fletcher, "A Simple Model for Predicting the Flux Distribution Through the Focal Plane of a Multifaceted-Concentrator Solar Furnace," Transactions of the American Society of Mechanical Engineers, Vol. 106, 104(1984).

5. Edward A. Fletcher, Frank J. Macdonald, and Dennis Kunnerth, "High Temperature Solar Electrothermal Processing II. Zinc from Zinc Oxide," Energy 10 12 1255-1272(1985).

6. Donald J. Parks, Kent L. Scholl, and Edward A. Fletcher, "A Study of the Use of $Y_2O_3$ Doped $ZrO_2$ Membranes for Solar Electrothermal and Solarthermal Separations," Energy <u>13</u>, 121-136 (1988).

7. Aldo Steinfeld and Edward A. Fletcher, "A Solar Receiver-Reactor with Specularly Reflecting Walls for High-

Temperature Thermoelectrochemical and Thermochemical Processes," Energy 13, 301-311 (1988).

8. Robert D. Palumbo and Edward A. Fletcher, "High Temperature Solar Electrothermal Processing III. Zinc from Zinc Oxide at 1200-1676K Using a Non-Consumable Anode," Energy 13, 319-332 (1988).

9. A. Steinfeld and Edward A. Fletcher, "Solar Energy Absorption Efficiency of an Ellipsoidal Receiver-Reactor with Specularly Reflecting Walls," Energy 13, 609(1988).

10. Kirk Nygren, Radoslav Atanasoski, William H. Smyrl, and Edward A. Fletcher, "Hydrogen and Sulfur from Hydrogen Sulfide V. Anodic Oxidation of Sulfur on Activated Glassy Carbon," Energy 14, in press, 1989.

g. Graduate students supported in whole or in part on this contract.

David Carlson, MS
Todd Kappauf, MS, PhD
Frank Macdonald, MS, PhD
Jean Murray, PhD
Robert Palumbo, MS,PhD
Aldo Steinfeld, working for PhD
Kent Scholl, working for MS

h. Post doctoral researchers supported in whole or in part on this contract.

Richard B. Diver
Todd Kappauf
Dennis Kunnerth
Donald Parks
Ludmila Stachovicz

i. Presentations at Topical or Scientific/Technical Society Conferences.

1. E.A. Fletcher, R.B. Diver, and J.E. Noring, "High-Temperature Oxide Electrolytes for the Splitting of Water--The ROC Process," Proceedings of the Conference on High Temperature Solid Oxide Electrolytes, August 16-17, 1983, BNL-51728, Vol 1, Brookhaven National Laboratory, Upton, Long Island, NY, October, 1983.

2. Edward A. Fletcher, "High Temperature Solar energy Research at The University of Minnesota," Proc. 1986 American Society of Mechanical Engineers Solar Energy Conference, Anaheim, California, April 14-17, 1986.

3. Edward A. Fletcher "High Temperature Solar Energy Research at the University of Minnesota--Past and Future," Invited lecture at the Second International Congress and Exhibition on Energy, June 5-10, 1988. Tiberias, Israel.

4. K. Nygren, W.H. Smyrl, E.A. Fletcher, and R.T. Atanasoski, "Electrolysis of Hydrogen Sulfide in Aqueous Alkaline Solutions," Paper No. 549 at the 173rd Annual Meeting of the Electrochemical Society, May 1988, Atlanta, Georga (presented by W.H. Smyrl).

j. Other invited presentations.

1. The Weizmann Institute of Science, Rehovot, Israel, "High Temperature Solar Thermochemical Research at The University of Minnesota," Sept. 17, 1984.

2. Study Panel Participant, Solar Energy Research Institute, Solar Thermal Research Needs Workshop, Kansas City, MO, October, 1984.

3. Study Panel Participant, Solar Energy Research Institute, Annual Conference, Lakewood, Colorado, February, 1985. February, 1985

4. Special Seminar at The Weizmann Institute of Science, Rehovot, Israel, "Recent Developments in High Temperature Solar Thermochemical and Thermoelectrochemical Research at The University of Minnesota," July, 1985.

5. "The Thermodynamics of Solar Processes," Solar Energy Research Institute, Annual Conference, Golden, Colorado, February, 1986.

6. "Reactor Experiments at The University of Minnesota," Third Meeting of the International Energy Association on Solar Fuels, Chemicals, and Energy Transport, Sandia National Laboratory, Albuquerque, NM, March 5-6, 1987,.

7. "Reactors, Receivers, and Windows for High Temperature Solarthermal Processes," Working Meeting of the International Energy Association on Solar Fuels, Chemicals, and Energy Transport, Sandia National Laboratory, Albuquerque, NM, February 2-3 1989.

k. ONR Technical Reports emanating from the contract.

1. "High Temperature Electrothermal Processing - Zinc from Zinc Oxide," Office of Naval Research Contract N00014-82K-0523, Technical Report No. 1, October 11, 1982, with Jon Noring.

2. "Hydrogen and Sulfur from Hydrogen Sulfide II. Ambient Temperature Electrolysis Using Oxidation of Hydrogen Sulfide by Air as the Prime Energy Source," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 2, April 15, 1983.

3. "Hydrogen and Oxygen from Water VI. Quenching the Effluent from a Solar Furnace," Office of Naval Research Contract N00014-82-K-0523, Technical Report No. 3, April 15, 1983, with R.B. Diver, S. Pederson, and T. Kappauf.

4. "High Temperature Electrolytes for the Splitting of Water-- The ROC Process," in Proceedings of the Conference on High Temperature Solid Oxide Electrolytes, August 16-17, 1983, BNL-51728, Vol 1, Brookhaven National Laboratory, Upton, Long Island, NY, October, 1983, Office of Naval Research Contract N00014-82k-0523, Technical Report No. 4, with R.B. Diver, and J.E. Noring.

5. "A Simple Model for Predicting the Flux Distribution Through the Focal Plane of a Multifacted-Concentrator Solar Furnace," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 5, with D. Carlson and R.B. Diver.

6. "High Temperature Solar Electrothermal Processing II. Zinc from Zinc Oxide," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 6, with Frank Macdonald and Dennis Kunnerth.

7. "High Temperature Solar Energy Research at The University of Minnesota," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 7.

8. "A Study of the Use of Y2 Doped ZrO2 Membranes for Solar Electrothermal and Solarthermal Separations," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 8, with D.J. Parks and K.L. Scholl.

9. "Reactor Experiments at the University of Minnesota," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 9.

10. "High Temperature Solar Electrothermal Processing III. Zinc from Zinc Oxide at 1200-1675K Using a Non-consumable Anode," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 10, with R.D. Palumbo.

11. "A Solar Receiver-Reactor with Specularly Reflecting Walls for High-Temperature Thermochemical Processes," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 11, with A. Steinfeld.

12. "Solar Energy Absorption Efficiency of an Ellipsoidal Receiver-Reactor with Specularly Reflecting Walls," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 12, with A. Steinfeld.

13. "Hydrogen and Sulfur from Hydrogen Sulfide V. Anodic Oxidation of Sulfur on Activated Glassy Carbon," Office of Naval Research Contract N00014-82k-0523, Technical Report No. 13, with K. Nygren, R. Atanasoski, and W.H. Smyrl.

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